Studies on the Interactions of Polyelectrolyte Mixture with Salt and Surfactant Ions in Aqueous Media

Summary of Research Work for the Award of Ph.D. Degree (Science) in Chemistry Department of Chemistry, Presidency University

Submitted by SudipaSantra

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Synopsis of the Thesis

Mixtures of polyelectrolytes and oppositely charged surfactants in solutions are characterized by complex and rich aggregation behavior [1-7]. The origin of this behavior lies in the strong interactions amongst the polyelectrolytes and surfactants present in these solutions. Subtle interplay of Coulombic forces between the polar heads of the surfactants and the charged polyion chains, and hydrophobic forces between the apolar tails of the surfactants drives the interactions in such systems.Due to the electrostatic interaction with oppositely charged ionic surfactants, polyelectrolytes can form complexes which modify the interfacial properties and affect the emulsion stability [8-11]. Extensive applications of polyelectrolyte-surfactant combinations for domestic, industrial, and technological purposes over the past decades [1,5,8,12]prompted the researchers to undertake comprehensive investigations on these systems over decades.

It is, however, worth noting that the systems consistingof polyelectrolytes and the so-called conventional surfactants have been extensively investigated [4,5,13-23].

Since polyelectrolytes modify the interfacial properties of surfactants, mixtures of polyelectrolytes should also do the same. However, they may either improve, or deteriorate the surface activity behavior of surfactants, or remain indifferent. Improved surface activity is beneficial for practical application of surfactants. However, till now, there has been no attempt to explore the influence of polyelectrolyte mixtures on the interfacial behavior of surfactants. In order to address this lacuna, we undertook a comprehensive study to investigate the influence of some selected binary mixtures of polyelectrolytes on the interfacial as well as the aggregation behavior of a surfactant using different experimental techniques. For this, we should also have a clear picture as to the polyion-counterion interactions in the individual and mixed polyelectrolyte systems. In particular, as a part of this study, we also characterized the subtle interactions prevailing in pure and mixed polyelectrolyte systems both in the absence and in presence of an added salt.

For the study, we selected two negatively charged polyelectrolytes – sodium carboxymethylcellulose and sodium alginate, two positively charged polyelectrolytes – poly(diallyldimethylammonium chloride) and poly(acrylamide-*co*-diallyldimethylammonium chloride), a salt (NaCl) and a surfactant – 1-decyl-3-methylimidazolium chloride. The results have been analyzed on the basis of the present-day-knowledge of polyelectrolyte and surfactant solutions.

Specifically, the works embodied in this thesis include:

1. Investigation on the transport and polyion-counterion condensation behavior of the polyelectrolytes sodium alginate, sodium carboxymethylcellulose, poly(diallyldimethyl-ammonium chloride) and poly(acrylamide-*co*-diallyldimethylammonium chloride) both in the absence and presence of a salt in aqueous solutions at different temperatures.
2. Investigation on the transport and polyion-counterion condensation behavior of the mixtures sodium alginate + sodium carboxymethylcellulose, and poly(diallyldimethyl-ammonium chloride) + poly(acrylamide-*co*-diallyldimethylammonium chloride) both in the absence and presence of a salt in aqueous solutions at different temperatures.

Sudipa Santra

3. Investigation on the aggregation and interfacial behavior of the surfactant (1-decyl-3-methylimidazolium chloride) in presence of each the polyelectrolyte individually in aqueous solutions as a function of temperature.
4. Investigation on the aggregation and interfacial behavior of the surfactant (1-decyl-3-methylimidazolium chloride) in presence of each the binary mixtures of the polyelectrolytes namely sodium alginate + sodium carboxymethylcellulose, and poly(diallyldimethyl-ammonium chloride) + poly(acrylamide-*co*-diallyldimethylammonium chloride) in aqueous solutions as a function of temperature.

Besides exploring the interactional features in the investigated polyelectrolyte mixture-surfactant systems, the present study is expected to help extend the fruitful use of these polyelectrolytes.

Chapter 1 provides a general introduction to polyelectrolytes and their counterion-condensation behaviour in solutions, surfactants and their interfacial and micellization properties, and polyelectrolyte-surfactant interactions. A brief review of the notable works in the fields of polyelectrolyte solution chemistry with particular reference to the condensation of counterions onto the polyions and those in the fields of surfactants and polyelectrolyte-surfactant systems have been given. Also various theories of solutions of polyelectrolytes and surfactants have been thoroughly discussed which have been used for the analyses of the experimental data in the following chapters.This is followed by an account of conductometry, tensiometry, viscometry, and spectrofluorimetry to investigate the interactions in polyelectrolyte and polyelectrolyte-surfactantsystems in aqueous solutions since these techniques have been employed to study the nature of polyelectrolyte-salt and polyelectrolyte-surfactant interactions in this dissertation.

Chapter 2provides an account of the counterion-condensation and related phenomena in aqueous solution of a naturally-occurring anionic polyelectrolyte sodium alginate in absence as well as in presence of sodium chloride using electrical conductivity as the probe. In particular, the variations of the counterion-condensation behavior as functions of polyelectrolyte concentration, added electrolyte concentration, and temperature were investigated. A phenomenological treatment of the data which considered the additivity of salt and polyelectrolyte conductivities the Debye-Hückel interactions using Manning's theoretical expressions for self-diffusion was performed [24,25]. The results indicated a marked departure from the additivity. The data were, therefore, analyzed on the basis of the de Gennes scaling model for the configuration of a polyion chain in semidilute solutions[26-28]. Counterion-dissociation reached its maximum in absence of the added salt, whereas counterion-condensation reached its maximum in presence of the highest amount of the added salt (Fig.1). In moderately saline media, however, counterion-condensation was initially found to increase with polyelectrolyte concentration which then gradually leveled off indicating confinement of counterions within the domains of polyion chains at higher polyelectrolyte concentrations. Results indicated the existence of alginate ions as flexible chains in aqueous solutions. A subtle balance of the influences of the effective monomer charge and the effective monomer size was found to play a pivotal role the polyion mobility. Possible conformational changes of the polyion chains caused by dilution led to changes in hydrodynamic resistance in the investigated solutions. The results also provided important insight as to the influence of the alterations of the hydration behavior of the counterions and the relative permittivity of the media on counterion-condensation in the investigated systems.

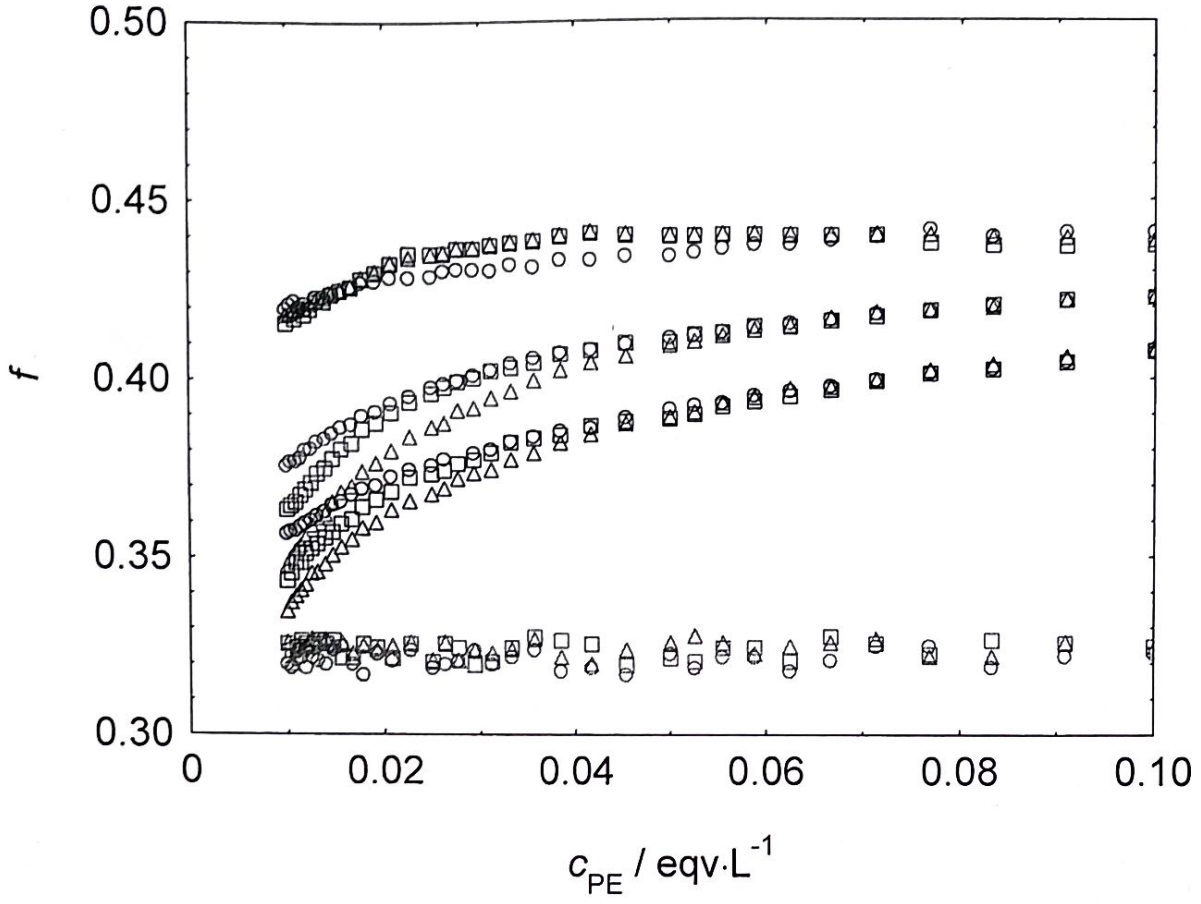

Fig. 1. Fraction of free counterions (f) in aqueous sodium alginate solutions as a function of polyelectrolyte concentration (c_{PE}) at different temperatures in absence (blue), and in the presence of 0.008 mol·L^{-1}NaCl (red), 0.020 mol·L^{-1}NaCl, (black), 0.100 mol·L^{-1}NaCl (pink). Symbols represent experimental values at 298.15 K (circles), 308.15 K (squares) and 318.15 K (triangles), whereas the lines are used to guide the eye.

Chapter 3 provides a description of a comprehensive study on the polycation charge and conformation poly(acrylamide-*co*-dimethyldiallylammonium chloride) with a moar mass of 250 kDa (comprising of 45 mass% of dimethyldiallylammonium chloride) performed in aqueous media without and with an electrolyte as a function of temperature. Use has been made of the scaling concepts of de Genne*set al.* [29] to analyse the electrical conductance-concentration. The results indicated that the charge on each polycation reduced from a value of ~ 450 in the maximally perturbed chain to ~ 100 in an unperturbed chain at 298.15 K when the copolymer concentration was ~ 0.06 monomol·L^{-1} (the highest concentration investigated). The intrinsic persistence length of the polycation (7.2 A^0) estimated from viscosity measurements using the worm-like coil model of polymer was found to be smaller than the average length of each repeating unit, indicating inherent flexibility of this copolymer. It is observed that in salt-free solutions polycations adopt a slightly stiff and extended conformation (upto around 4 repeating units) because of intra-chain electrostatic repulsions at 298.15 K when the copolymer concen-

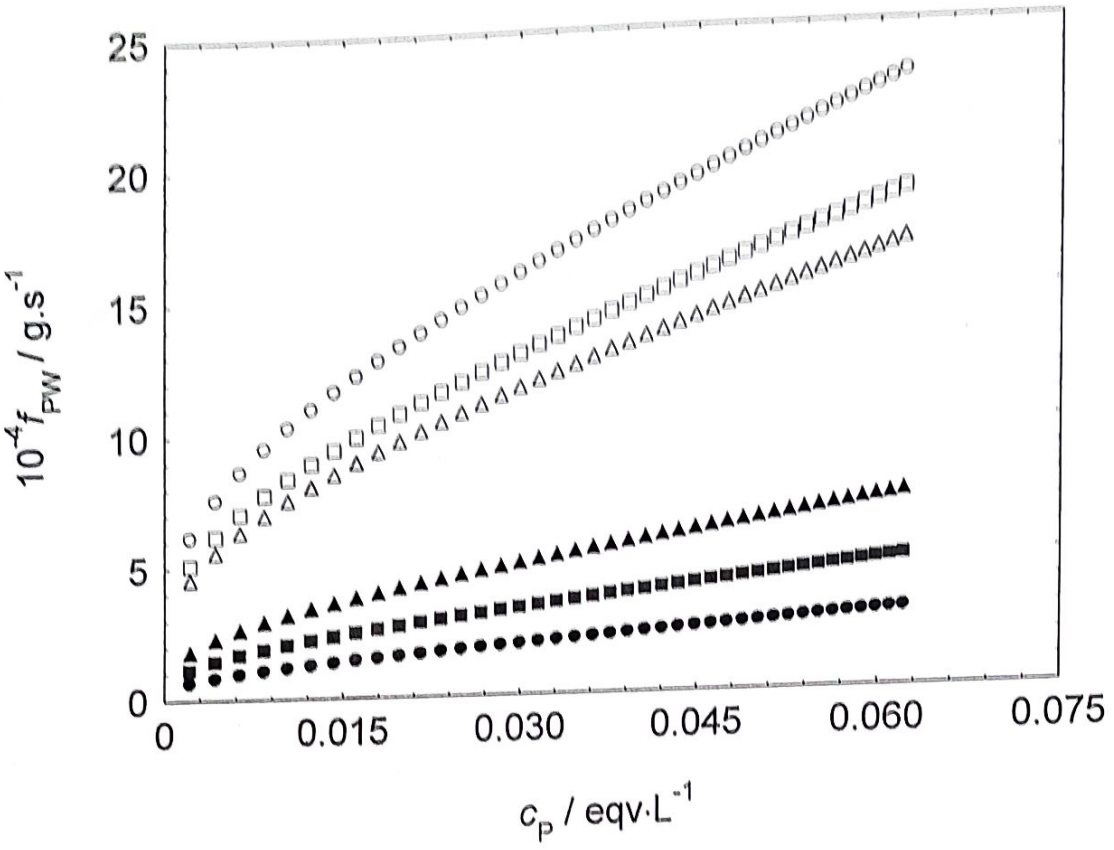

Fig. 2. Variation of the monomer-solvent friction coefficient (f_{PW}) of poly(acrylamide-*co*-diallyldimethylammonium chloride) in aqueous solutions with the concentration of the copolymer (c_P) in absence (open symbols) and in the presence of 0.5 mol·L^{-1}NaCl at 298.15 K (blue), 308.15 K (red), and 318.15 K (black).

tration was ~ 0.002 monomol·L^{-1} (the lowest concentration investigated). The variation of the coefficient of friction of the monomer with polymer concentration is found to be governed by theeffect of chain charges over and above that of the chain stiffness (**Fig. 2**); in the unperturbed state, however, the effect of chain charges is the sole determinator. This study sheds lights on the dependence of polycation charge and conformation with the concentration of copolymer, temperature, and salinity of the medium.

Chapter 4 reports onthe studies on the counterion condensation in the binary mixtures of two negatively-charged polyelectrolytes (sodium alginate and sodium carboxymethylcellulose by conductance measurement in aqueous medium. The investigation has been carried out both in the absence and in presence of an added salt (NaCl). The specific conductance vs.polyelectrolyte concentration data were analyzed in the light of the scaling argument for the conformation of polyion chains in solutions to quantify the fractions of free counterions as described in chapters 2 and 3. Effects of polyelectrolyte concentration, composition of the mixture, and solution temperature on the condensation of counterions have been investigated to explore polyion-

counterion interaction, and inter- and intra-chain interactions in these polyelectrolyte mixtures. This investigation revealed that the extent of counterion condensation is significantly influenced by themixture composition, the polyelectrolyte concentration and the temperature. Addition of salt considerably reduced the fraction of free counterions in the binary polyelectrolyte solutions (**Fig. 3**). This study establishes a definite dependence of the polyion-counterion interactions on total polyelectrolyte concentration, which is, however, not in agreement with what concluded earlier from the dependence of the fast diffusion coefficient on total polyelectrolyte concentration or on the composition of the mixtures of polyelectrolyte with different molecular weights in aqueous sodium polystyrenesulfonate mixtures using dynamic light scattering measurements [30]. However, the conclusions arrived at in this study agrees with the results on mixed sodium polystyrenesulfonate systems both in water and methanol-water media using conductometry[31,32]. Evaluation of the polyion transference numbers provided important information as to the direction of the motion of the counterions under the action of the applied electric field.The counterion dissociation of polyelectrolytes is extremely important and pivotal in determining the charge state of polyions and the interaction between polyions and counterions.

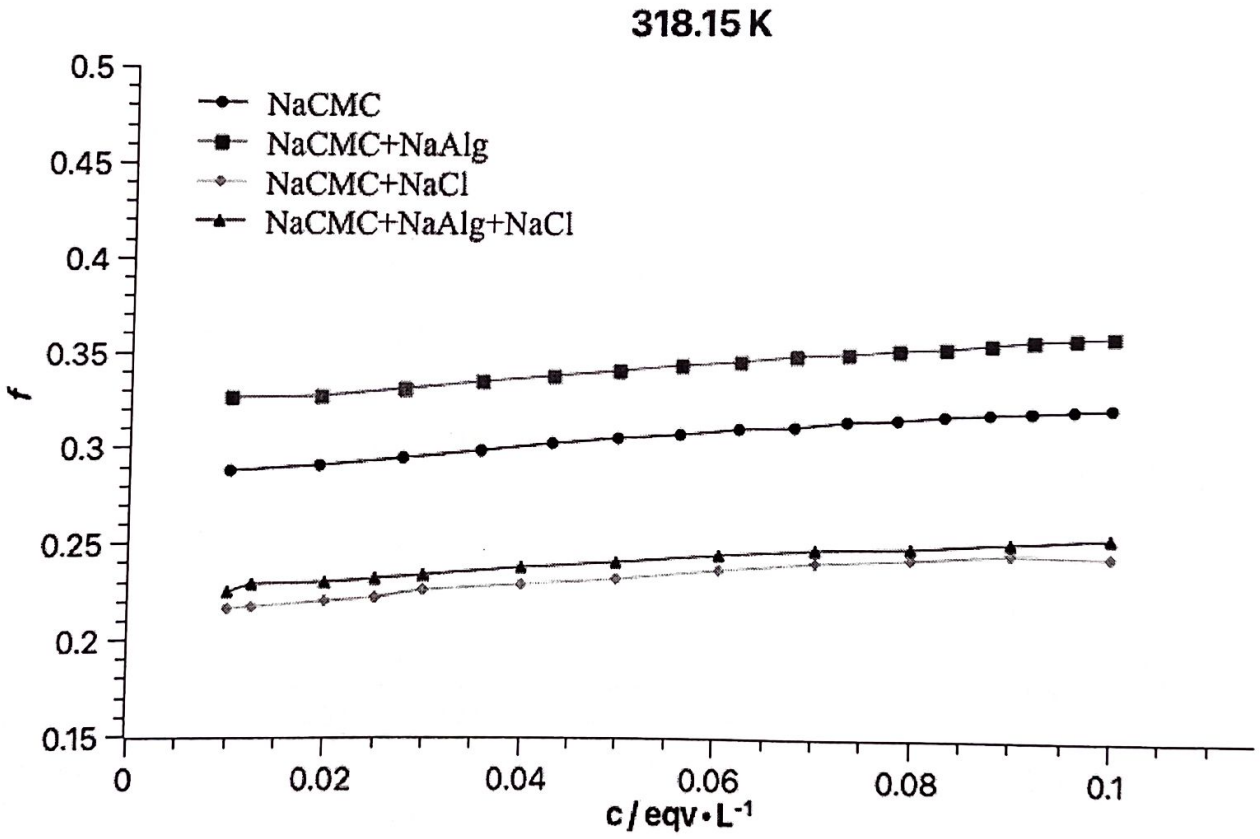

Fig. 3. Fractions of free counterions (*f*) in aqueous solutions of sodium carboxymethylcellulose (NaCMC), sodium carboxymethylcellulose + NaCl, sodium carboxymethylcellulose + sodium alginate, and sodium carboxymethylcellulose + sodium alginate + NaCl solutions at 318.15 K.

In **Chapter 5**, polyion charges have been estimated via conductometry in aqueous binary mixtures of two cationic polyelectrolytes poly(diallyldimethylammonium chloride) and poly(acrylamide-*co*-diallyldimethylammonium chloride) as well as in pure poly(diallyldimethyl-chloride) solutions as a function of temperature and polyelectrolyte concentration. Analyses of conductance - concentration data have been performed on the basis of the scaling description of the polyelectrolyte configuration. The effective charges on the polyionchains have been found to depend on the polyelectrolyte concentration, particularly in the low concentration region, and finally reach a plateau as the concentration is subsequently increased (**Fig. 4**). This study also revealed that the degree of counterion condensation is altered appreciably with the temperature. Analyses of the results indicate that the mixing of these two polyelectrolytes is non-ideal. The roles of the relative permittivity of the medium, the screening of chain charges, the coiling of polyion chains, and the desolvation of counterions in governing the process of counterion-condensation have been critically assessed. An empirical equation to describe the extensive array of the fraction of free counterions obtained in this study has been proposed. This equation has been shown to be very useful, and the absolute average difference or the standard deviation between the experimental and calculated values was always found to be within ±0.01.

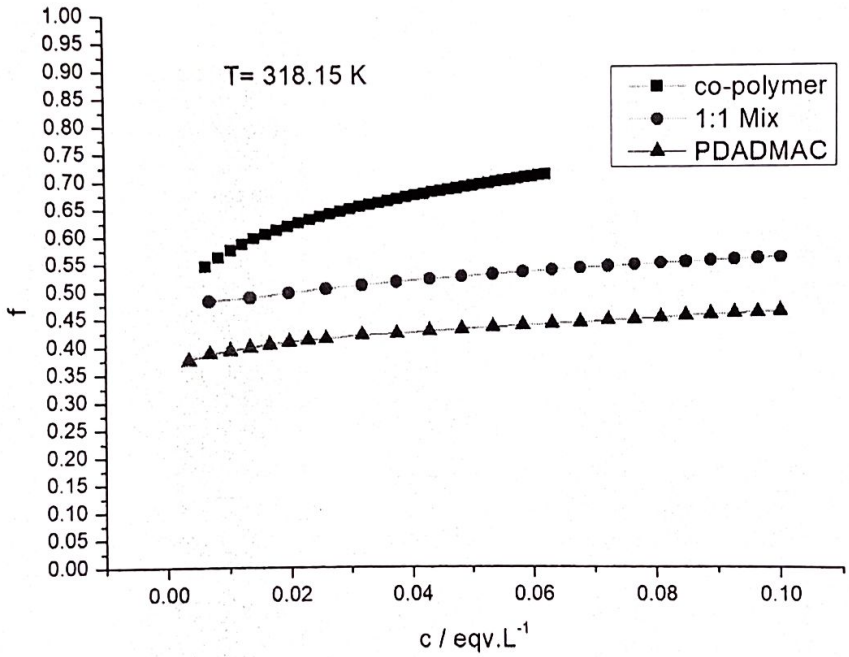

Fig 4. Comparison of the fraction of free counterions in aqueous solutions of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(acrylamide-*co*-diallyldimethylammonium chloride) (co-polymer) and a 1:1 (monomol ratio) mixture of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(acrylamide-*co*-diallyldimethylammonium chloride) (co-polymer) at 318.15 K.

Chapter 6 pertains to a study exploring the influence of sodium carboxymethylcelulose, sodium alginate, and sodium carboxymethylcelulose + sodium alginate binary mixtures on the aggregation phenomena of a surfactant 1-decyl-3-methylimidazolium chloride in aqueous solutions using electrical conductivity, surface tension measurements and fluorescence measurements using pyrene as a probe (a representative conductivity profile and a representative tensiometric profiles are shown in **Fig. 5**. Two characteristic concentrations, namely the critical aggregation concentration and polymer saturation concentration, before free 1-decyl-3-methylimidazolium chloride micelles appear in these solutions, have been identified using surface tension measurements. Conductivity and fluorescence studies indicated only one critical concentration namely the critical micelle concentration (*cmc*). Effects of temperature, polyelectrolyte concentration, and the charge density parameter of the polyelectrolyte molecules on the self-aggregation of the 1-decyl-3-methylimidazolium chloride have been discussed to elucidate the interactions in sodium carboxymethylcelulose + 1-decyl-3-methylimidazolium chloride, sodium alginate + 1-decyl-3-methylimidazolium chloride solutions, and sodium carboxymethylcelulose + sodium alginate + 1-decyl-3-methylimidazolium chloride solutions. The thermodynamic parameters formicellization of 1-decyl-3-methylimidazolium chloride were estimated in these

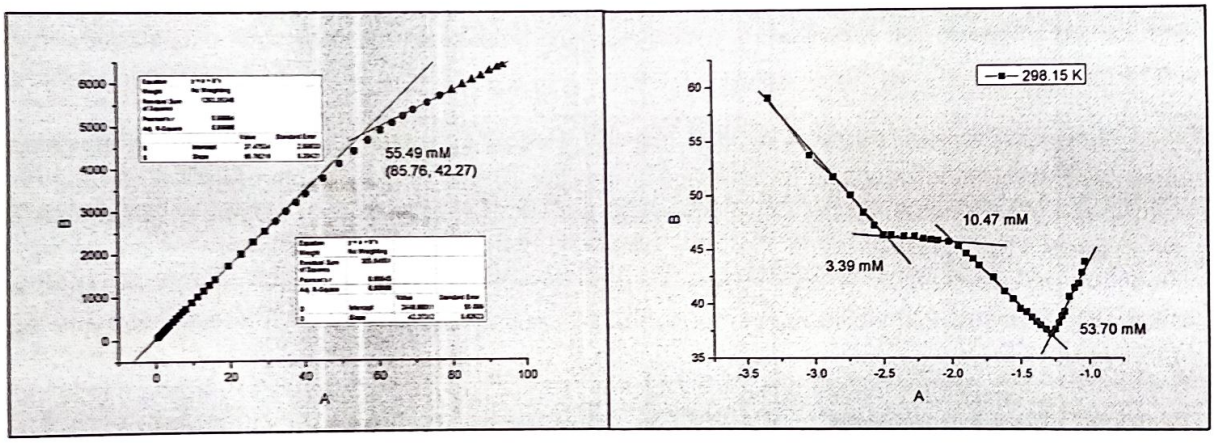

Fig. 5. [Left panel] Specific conductivity (B/μS.cm^{-1}) vs. concentration (A/monomol.L^{-1}), and [Right panel] surface tension (γ/dyne.cm^{-1}) vs. concentration (A/monomol.L^{-1}) profiles for aqueous solutions of sodium carboxymethylcelulose + sodium alginate + 1-decyl-3-methylimidazolium chloride solutions (1:1 monomol ratio) at 298.15 K.

complex fluids. The observed enthalpy-entropy compensation effect in 1-decyl-3-methylimidazolium chloride in the pure and mixed polyelectrolyte systems provided important insight as to how micellization processes are governed by the bulk structural property of the solution with respect to that of the water. Evaluation of the interfacial parameters indicated a considerable change in the surface activity of the surfactant in presence of the mixed polyelectrolytes compared to the pristine ones.

In**Chapter 7,** we have studied the influences of poly(diallyldimethyl-ammonium chloride), poly(acrylamide-*co*-diallyldimethylammonium chloride) as well as their binary mixtures on the aggregation, interfacial, and thermodynamic phenomena of the surfactant 1-decyl-3-methylimidazolium chloride with a view to explore the effects of mixed polyelelectrolyte systems viz-a-viz the pure ones and the temperature. Conductometry, tensiometry, and spectrofluorimetry have been employed. Surface activity of 1-decyl-3-methylimidazolium chloride was found to greatly modified in presence of the mixed polyelectrolytes. Evaluation of the Gibbs minimum free energy demonstrates a poorer thermodynamic stability of the interfacial growth of the 1-decyl-3-methylimidazolium chloride molecules as the temperature is elevated. The pC_{20}values provided a comparative measure of theinterfacial adsorption in these systems within the investigated temperature range. Two characteristic concentrations, e.g., the critical aggregation concentration (*cac*) and polymer saturation concentration (*psc*), prior to the appearance of free 1-decyl-3-methylimidazolium chloride micelles above the critical micellar concentration (*cmc*) in each of the mixed solutions have been identified. Micellization of 1-decyl-3-methylimidazolium chloride has been found to be thermodynamically spontaneous in presence of the pure and mixed polyelectrolyte systems. As the temperature increases micellizationhas been found to become more spontaneous. The geometrical shapes of 1-decyl-3-methylimidazolium chloride micelles in presence of the pure and mixed polyelectrolytes have been predicted to be spherical irrespective of the experimental temperatures. The results have been discussed to elucidate the polyelectrolyte-surfactant interactions in presence of mixed surfactants considering diverse forces prevailing in these mixed systems.

Finally in the concluding chapter [**Chapter 8**] we will underscore the efficacies of the methodologies employed in this study to unravel the nature of such complex fluids. Future objectives and potential applications will also be discussed based on the results obtained in this study on the interactions of polyelectrolyte mixtures with salt and surfactant ions in aqueous media.

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List of Papers Published.

1. S. Santra, Bijan Das, Counterion-binding and related phenomena in sodium alginate-sodium chloride-water ternary systems: A conductometric study, *Journal of Molecular Liquids*, 296, 111930, **2019**. 10.1016/j.molliq.2019.111930.
2. S. Santra, A. Banerjee, B. Das, Polycation charge and conformation of aqueous poly(acrylamide-*co*-diallyldimethylammonium chloride): Effect of salinity and temperature, *Journal of Molecular Structure*, 1247, 131292, **2022**. https://doi.org/10.1016/j.molstruc.2021.131292.
3. R. De, A. Banerjee, S. Santra& B. Das, Counterion dissociation in mixtures of sodium polystyrenesulfonate with different molar masses in aquo-organic media, *New Journal of Chemistry*, 46 (48), 23245-23253, **2022**. 10.1039/D2NJ04903A.

List of Conferences Attended

1. International Conference on Advancement in Science & Technology (ICAST-2018), Visva-Bharati, 3-4 September, 2018: Poster Title: Salt Induced Counterion Condensation and Related Phenomena in Sodium Alginate-Sodium Chloride-Water Ternary Systems.
2. "Spectrum 2019" 2nd International Students Conference on Innovations in Science and Technology, IEM, Kolkata, 7-9 March, 2019. Poster Title: Studies on the Interactions in Binary Mixture of Polyelectrolytes : Effect of Mixture Composition and Concentration on Counterion Condensation [Best Poster Award].
3. International Symposium on Recent Advances in Chemistry and Material Sciences (2019), SINP, Kolkata, 2-3 August 2019. Poster Title: Counterion-Condensation of PolydiallyldimethylammoniumChloride (PDADMAC) in Aqueous Solution: A Scaling Theory Approach.
4. 19th National Conference on Surfactants, Emulsions and Biocolloids (NATCOSEB-XIX), Amity University, Kolkata, 18-20 October 2019. Poster Title: Studies on the Interactions in binary mixture of sodium carboxymethylcellulose (NaCMC) with different molecular weights.

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SL. NO. Science/2017/11

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Certificate of Enrollment

This is to certify that upon approval by the Ph.D. Committee of the Department of CHEMISTRY and confirmation by the Faculty Doctorate Committee, and subsequently followed by submission of fees, SUDIPA SANTRA vide Enrolment No. PU/PHD/CHEM/2017/011 has been enrolled for the Ph.D. Programme of the Department of CHEMISTRY, Presidency University, Kolkata and course work starting from ***SEPTEMBER, 2017.***

Head of the Department	Dean of Faculty	The Registrar
Head Department of Chemistry Presidency University Kolkata-700073	Dean Faculty of Natural and Mathematical Sciences Presidency University, Kolkata	Registrar Presidency University Kolkata

Date: 20th Sept. 2017

Self attested by
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SL. NO. Science/S-75/19.

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REGISTRATION CERTIFICATE

This is to certify that Ms. Sudipa Santra, d/o Sanatan Santra, has been granted registration for the Ph.D. Programme in the **Department of Chemistry** of Presidency University, Kolkata in terms of the Regulations (No. 4) for the Degree of Doctor of Philosophy (Ph.D.).

Registration Number: **R-17RS205210110**

Date of Registration: **10th July, 2018**

Title of the thesis: "Studies on the Interactions of Polyelectrolyte-mixture with Salt and Surfactant Ions in Aqueous Media"

This registration shall remain valid for five years with effect from the date of registration as indicated above.

Registrar

Self attested by
Sudipa Santra

Date: 29th January 2019

PRESIDENCY UNIVERSITY
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Presidency University

Hindoo College (1817-1855), Presidency College (1855-2010)

Ref. No.: PU/FCS/542/PhD/comm/2024

Date: 24/07/2024

To
Ms. Sudipa Santra (Registration Number– R-17RS205210110 dated 10/07/2018)
Department of Chemistry
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Sub: Extension of validity of PhD Enrollment

Dear Scholar,

The Departmental PhD Committee of the Department of **Chemistry**, recommended the following extention of validity of PhD Enrollment till **9th July, 2025 (Second and last Extension)**, in its meeting dated 05.07.2024. The same has been approved by the competent authority subject to ratification in the next Doctorate Committee.

Best wishes

24/07/2024

Secretary,
Faculty Councils

Copy to:
Dr. Bijan Das (Supervisor)
HOD (Chemistry)
Finance Officer

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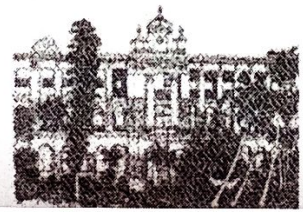
Sudipa Santra



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Counterion-binding and related phenomena in sodium alginate-sodium chloride-water ternary systems: A conductometric study

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Counterion-binding
Effective monomer charge and size

ABSTRACT

Counterion-binding and related phenomena in aqueous solution of the naturally-occurring anionic polyelectrolyte sodium alginate have been explored in absence as well as in presence of sodium chloride using electrical conductivity as the probe. In particular, the variations of the counterion-binding behavior as functions of polyelectrolyte concentration, added electrolyte concentration, and temperature were investigated. A phenomenological treatment of the data which considered the additivity of salt and polyelectrolyte conductivities taking into account the Debye-Hückel interactions using Manning's theoretical expressions for self-diffusion was performed. The results indicated a marked departure from additivity. The data were, therefore, analyzed on the basis of the de Gennes scaling model for the configuration of a polyion chain in semidilute solutions. Counterion-dissociation reached its maximum in absence of the added salt, whereas counterion-binding reached its maximum in presence of the highest amount of the added salt. In moderately saline media, however, counterion-binding was initially found to increase with polyelectrolyte concentration which then gradually leveled off indicating confinement of counterions within the domains of polyion chains at higher polyelectrolyte concentrations. Results indicated the existence of alginate ions as flexible chains in aqueous solutions. A subtle balance of the influences of the effective monomer charge and the effective monomer size played a pivotal role the polyion mobility. Possible conformational changes of the polyion chains caused by dilution led to changes in hydrodynamic resistance in the investigated solutions. The results also provided important insight as to the influence of the alterations of the hydration behavior of the counterions and the relative permittivity of the media on counterion-binding in the investigated systems.

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1. Introduction

Alginates are naturally-occurring water-soluble polysachharides found abundantly in the cell walls of brown algae [1–3]. Alginates are linear polymers of two monomeric units, β-(1–4)-D-mannuronic acid (M) and α-L-guluronic acid (G) (Scheme 1). They can be classified as polyelectrolytes - a special class of polymers - which dissociate in polar media to yield a polyion or macroion and a large number of oppositely charged ions referred to as counterions. Alginates find widespread applications as thickeners, gelling agents, and colloidal stabilizers [4]. The most useful property of these biopolymers is their ability to react with cations to produce gels or insoluble polymers [5,6]. Counterion-binding onto the polyion chains should be taken into account while considering the interaction of alginates with other cations. Elucidation of the interactions in solutions of alginates particularly in presence of cations is, therefore, of utmost importance not only to understand their mechanism of action in the areas of application, but also to reveal the fundamental chemistry prevailing in these solutions.

The purpose of this study is to explore counterion-binding and transport properties of aqueous solutions of sodium alginate in absence as well as in presence of an added salt with particular reference to the effect of sodium alginate concentration, concentration of the added salt, and temperature using electrical conductivity as the probe. Analyses of the experimental results using the scaling description of Dobrynin et al. [7] helped us recover the extent of counterion-binding and explore the interactions in these systems in a quantitative manner.

2. Experimental

2.1. Materials

Sodium alginate and sodium chloride (NaCl) were purchased from Sigma-Aldrich. The average molecular weight of the sample (108200 g · mol^{-1}) was estimated from the intrinsic viscosity value determined in presence of 0.1 mol · L^{-1} NaCl aqueous solution at 298.15 K using the Mark-Houwink equation with the constants obtained from the

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Polycation charge and conformation of aqueous poly(acrylamide-*co*-diallyldimethylammonium chloride): Effect of salinity and temperature

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ABSTRACT

A comprehensive study on the polycation charge and conformation poly(acrylamide-*co*-dimethyldiallylammonium chloride) with a moar mass of 250 kDa (comprising of 45 mass% of dimethyldiallylammonium chloride) has been performed in aqueous media without and with an electrolyte as a function of temperature. Use has been made of a model of polyelectrolyte conductivity developed by Colby et al. [10] to analyze the electrical conductance-concentration data. The results indicated that the charge on each polycation reduced from a value of ~ 450 in the maximally perturbed chain to ~ 100 in an unperturbed chain at 298.15 K when the copolymer concentration was ~ 0.06 monomol·L^{-1} (the highest concentration investigated). The intrinsic persistence length of the polycation (7.2 A^0) estimated from viscosity measurements using the worm-like coil model of polymer was found to be smaller than the average length of each repeating unit, indicating inherent flexibility of this copolymer. It is observed that in salt-free solutions polycations adopt a slightly less flexible and extended conformation (upto around 4 repeating units) because of intra-chain electrostatic repulsions at 298.15 K when the copolymer concentration was ~ 0.002 monomol·L^{-1} (the lowest concentration investigated). The variation of the coefficient of friction of the monomer with polymer concentration is found to be governed by the effect of chain charges over and above that of the chain stiffness; in the unperturbed state, however, the effect of chain charges is playing the pivotal role. This study sheds lights on the dependence of polycation charge and conformation with the concentration of copolymer, temperature, and salinity of the medium.

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1. Introduction

Poly(acrylamide-*co*-dimethyldiallylammonium chloride) is a water-soluble cationic copolymer of acrylamide and dimethyldiallylammonium chloride (Scheme 1). It belongs to a distinct class of polymeric species, known as polyelectrolytes which when dissolved in polar solvents dissociate to yield polyions along with oppositely charged counterions [1,2]. The polyions and its counterions are strongly correlated, and it is this correlation that confers charge on the polyions. The above-mentioned polymer finds widespread use in papermaking, cosmetic formulations, treatment of wastewater, printing, mining and dyeing of textiles, daily chemical industry, slurry dehydration, etc. [3]. In these applications, the behavior of this cationic polyelectrolyte plays a pivotal role. The structure of polyelectrolytes is governed by two intricately related parameters, namely the charge and the size of the polyion. These two key parameters affect the hydrodynamic and frictional behavior of polyelectrolytes in solution. Thus, quantification of the charges and the sizes of these polycations would help elucidate their structural characteristics. Such characterization should play a crucial role in the modulation of the performance of poly(acrylamide-*co*-dimethyldiallylammonium chloride) in its applications. In this regard, electrical conductivity of this copolymer solution may be conveniently exploited as it monitors and quantitates the movement of the charged entities in solutions and could provide important insight into the structure of this polymer. The size of the polyion chains can, on the other hand, be estimated from viscosity measurements in conjunction with the information on the polyion charge to be obtained from conductometry.

The objective of the present work is, therefore, to shed light on the charge and conformation of the polycation of the cationic copolymer poly(acrylamide-*co*-dimethyldiallylammonium chloride) in aqueous solutions in salt-free and salt solutions. The influence of polymer concentration, added salt concentration, and temperature on the charge, size, and flexibility of the polyion chains will also

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Counterion dissociation in mixtures of sodium polystyrenesulfonate with different molar masses in aquo-organic media

Ranjit De,[a] Arnab Banerjee,[b] Sudipa Santra[b] and Bijan Das *[b]

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The counterion dissociation of polyelectrolytes is extremely important and pivotal in determining the charge state of polyions and the interaction between polyions and counterions. Polyion charges have been estimated *via* conductometry using sodium polystyrenesulfonate as a model under various experimental conditions. Analyses of conductance–concentration data have been performed on the basis of the scaling description of the polyelectrolyte configuration. The effective charges on the polystyrenesulfonate chains have been found to depend on the polyelectrolyte concentration, particularly in the low concentration region, and finally reach a plateau as the concentration is subsequently increased. This study also revealed that the degree of counterion condensation is altered appreciably with the composition of the polyelectrolyte mixture, the relative permittivity of the medium and the temperature. The roles of the relative permittivity of the medium, the screening of chain charges, the coiling of polyion chains, and the desolvation of counterions in governing the process of counterion condensation have been critically assessed. An empirical equation to describe the extensive array of the fraction of free counterions obtained in this study has been proposed. This equation has been shown to be very useful, and the absolute average difference or the standard deviation between the experimental and calculated values was always found to be within ±0.01.

1. Introduction

A polyelectrolyte is a charged macromolecule that dissociates in a polar medium to produce a charged chain, referred to as a polyion, along with a large number of oppositely charged counterions. The strong electric field exerted by the polyion gives rise to a distinct spatial correlation of the counterions around the polyion chain. This polyion–counterion correlation becomes directly apparent when one considers the electrical conductivity of polyelectrolyte solutions. The influence of this correlation of the counterions with the polyion can be conveniently expressed *via* the degree of counterion condensation onto the polyion chain, which is quantified as the fraction of condensed counterions (f_c), or by the fraction of free counterions (f), defined as $f = 1 - f_c$. In particular, the degree of counterion condensation, and hence the charge on the polyions and a measure of their interactions with the counterions can be obtained by measuring the electrical conductivity of polyelectrolyte solutions, since the electrical conductivity takes into account the movement of the charged entities in solution. Polyion charges have been shown to depend on the polyelectrolyte concentration, temperature, medium, and the added electrolyte.[1–6] Although the counterion-condensation behavior of single polyelectrolytes has been extensively investigated,[3,4,6–9] the behavior of multicomponent polyelectrolyte solutions has not really been considered so far, with the exception of only a few reports[10–12] on binary mixtures of sodium polystyrenesulfonate (with different molar masses) in aqueous solutions using different experimental techniques, namely conductometry and light scattering measurements. The conductivity study revealed that the extent of counterion condensation, and hence the polyion–counterion interactions, are influenced appreciably by the composition of the polyelectrolyte mixture, the polyelectrolyte concentration and the temperature. Previous DLS studies on binary mixtures of sodium polystyrenesulfonate with different molar masses in aqueous solutions demonstrated the coupled diffusion of polyions and counterions, which has been shown to be invariant with the total concentration of the polyelectrolyte, the composition of the mixture, and the molar masses of the two components.[11] The invariance of the coupled diffusion of polyions and counterions should imply an invariance of the polyion–counterion interactions. It is therefore evident that the nature of the polyion–counterion interaction in mixed

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Sudipa Santra

International Conference on Advancement in Science & Technology

(ICAST-2018)

3rd & 4th September, 2018

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Organized by

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participated in the conference and presented a poster.

Prof. Ashis Chattacharjee

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Sudipa Santra

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Studies On The Interactions In Binary Mixture Of Polyelectrolytes: Effect Of The Mixture Composition And Concentration On Counterion-Condensation

in Spectrum 2019 organized by Institute of Engineering & Management, Kolkata in collaboration with The Institution of Engineers (India) from 7th - 9th March, 2019 at IEM, Management House, Kolkata-91.

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Sudipa Santra

Arun Kumar Dar
Chairman, Spectrum 2019
Institute of Engineering

Kajal Ganguly
Kajal Ganguly
Convener, Spectrum 2019
Institute of Engineering

Prabir
Prabir Kumar
HOD, Basic Science
Institute of Engineering

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Sudipa Santra

3rd August, 2019
Kolkata

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Honorary Secretary
Indian Chemical Society

Professor Dulal C. Mukherjee
President
Indian Chemical Society

Professor Susanta Lahiri
Head, Chemical Sciences Division
Saha Institute of Nuclear Physics

Sudipa Santra

P. C. Ray Memorial International Conference

on

Contemporary Ideas, Innovations & Initiatives in Chemical Sciences

CI3CS-2023

CERTIFICATE OF PARTICIPATION

Presented to

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for actively participating/presenting a poster/~~an oral~~ at P. C. Ray Memorial International Conference on "Contemporary Ideas, Innovations & Initiatives in Chemical Sciences" held at the Department of Chemistry, Presidency University, Kolkata on 23rd & 24th August 2023.

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AMITY UNIVERSITY — KOLKATA —

18-20th October, 2019

Jointly Organized by

Department of Chemistry, Amity University Kolkata

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Indian Society for Surface Science and Technology , Jadavpur University, Kolkata

This is to Certify that Ms. Sudipa Santra *has attended the 19th NATIONAL CONFERENCE ON SURFACTANTS, EMULSIONS AND BIOCOLLOIDS (NATCOSEB-XIX) as Chairperson/ Invited speaker/oral presenter/ poster presenter and has presented his/her research entitled*

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has actively participated and presented a poster in a One Day National Symposium on Frontiers in Chemistry: from Fundamentals to Application *organized by the Department of Chemistry, Presidency University, Kolkata on 28th March, 2023.*

President

Secretary

Sudipa Santra

Dibyendu Mallick

Convenor

PRESIDENCY UNIVERSITY
DEPARTMENT OF CHEMISTRY
KOLKATA

Report on the pre-submission seminar for Ph.D.

1	Name of the candidate	Sudipa Santra
2	Department	Chemistry
3	Title of the thesis	"Studies on the Interactions of Polyelectrolyte Mixture with Salt and Surfactant Ions in Aqueous Media"
4	Date of receipt of 5000 word summary by the convenor	08/05/2025
5	Date of seminar presentation	19/5/2025

Bijan Das.

Signature of the supervisor

Date: 19/05/2025

Signature of the co-supervisor (if any)

Date:

This is to certify that Sudipa Santra (name of the candidate) presented her work in a departmental seminar in defense of his synopsis of thesis in presence of Ph.D committee, Faculty members and Research Scholars/MA/M.Sc/BA/B.Sc Students.

(Signature of the Convenor & members of the Departmental Ph.D Committee)

1. Prof. Bijan Das (Chairperson) Bijan Das 19/05/25
2. Prof. Arnab Halder (Head and convener) Arnab Halder 19/5/25
3. Prof. Sujoy Baitalik (External Member)
4. Prof. Chhanda Mukhopadhyay (External Member) Chhanda Mukhopadhyay 19/05/25
5. Prof. Arabindya Nayak (Member) 19/5/25
6. Dr. Dhruba Prosad Chatterjee (Member)
7. Dr. Adity Bose (Member) Adity Bose 19/5/25

Report on the performance of the candidate:

The presented work may be allowed to be submitted in the form of a thesis. The detailed report is attached as a separate sheet.

Report on the presubmission seminar delivered by Sudipa Santra, research Scholar, registration Number R-17RS205210110 dated 10-07-2018, Department of Chemistry, Presidency University, Kolkata 700073 as a prerequisite for submission of his Ph.D thesis entitled: "Studies on the Interactions of Polyelectrolyte Mixture with Salt and Surfactant Ions in Aqueous Media".

Sudipa Santra, Research Scholar, registration Number R-17RS205210110 dated 10-07-2018, Department of Chemistry, Presidency University, Kolkata 700073 made a power point presentation (in digital format), in an open seminar, in front of Departmental Ph.D committee on this day at 3:00 p.m. in the Department of Chemistry, Presidency University, Kolkata. She successfully defended all the queries made by the members of the Ph.D. committee as well as the audience. She has published in total two papers in peer reviewed international journals and attended six national and international seminars related to her thesis. She has fulfilled the required criteria for the submission of thesis. The volume and quality of work is highly satisfactory for submission of the thesis. She has completed his course works too. Based on her performance in this open seminar in which she presented her synopsis of research work (5000 words) committee strongly recommends that Sudipa Santra be allowed to submit her thesis for the Ph.D Degree in Science.

Signature of the Members of the Committee:

1. Prof. Bijan Das (Chairperson) Bijan Das. 19/05/25
2. Prof. Arnab Halder (Head and convener) Arnab Halder 19/5/25
3. Prof. Sujoy Baitalik (External Member)
4. Prof. Chhanda Mukhopadhyay (External Member) Chhanda Mukhopadhyay 19/05/25
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